

RINSING FORMULATION FOR TEXTILES

The present invention relates to an improved formulation intended for the rinsing of textile fiber articles, comprising a hydrophobic active substance 5 comprising a solid or liquid, particulate organic or organosilicon material.

It is known to use hydrophobic organic or organosilicon materials in textile rinsing compositions.

10 Patent US-A-4,818,242 describes an aqueous rinsing formulation which facilitates ironing, comprising a silicone oil cationically dispersed in water, a fatty acid-polyamine condensate, and a cationic film-forming agent.

15 Patent US-A-4,923,622 proposes rinse compositions comprising an emulsifiable concentrate which comprises cationic surfactants and an oil capable of exhibiting lubricating properties with regard to textiles to be treated, such as mineral oils and vegetable oils

20 containing 8 to 22 carbon atoms, and fatty acid esters.

The Applicant has found that the addition, to a formulation comprising particles of insoluble organic or organosilicon hydrophobic active substance and intended for the rinsing of textile fiber articles, of 25 a small amount of an appropriately selected soluble vehicle for said active substance makes it possible to improve significantly the deposition of particles on

the surface of said articles and hence to confer notable benefits on said articles, such as benefits of lubrication, of softness to the touch, of antiwrinkle properties and/or easy-iron properties and/or soil 5 release properties, and of abrasion resistance.

The invention first provides a formulation (F) intended for use in an operation of rinsing (R) textile fiber articles (S) by means of an aqueous or aqueous-alcoholic medium (MR), said formulation (F) 10 - comprising at least one active substance (A) comprising at least one solid or liquid organic or organosilicon material in particulate form and a vehicle (V) comprising at least one organic polymer, capable of taking said active substance (A) to the 15 surface of said textile fiber articles (S) in the rinsing operation (R),

- in the form:

- of a stable dispersion, with a pH of from 2 to 5, of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) comprising 20 said vehicle (V), or
- in a solid form obtained by drying said dispersion,

the nature of the active substance (A), of the aqueous or aqueous-alcoholic medium (MAV), and of the vehicle 25 (V) being such that

* the active substance (A)

- is insoluble in the medium (MAV),
- has an overall zero or cationic charge in the medium (MAV),
- is stabilized in the medium (MAV) by means of a cationic surfactant (TAC), it being possible for said cationic surfactant (TAC) to be wholly or partly replaced by a nonionic surfactant when the material constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV),
- remains insoluble in the rinsing medium (MR);
- the vehicle (V)
 - is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
 - has an overall cationic or zero ionic charge in the medium (MAV),
 - at the pH of the rinsing operation in the rinsing medium (MR) is capable of developing anionic charges in sufficient quantity to destabilize the active substance (A) in the rinsing medium (MR). The formulation according to the invention is intended for use equally for implementing a washing machine rinsing operation as a hand rinsing operation.

This operation is commonly carried out at a pH which can range from 5.5 to 8 (pH of the supply circuit water); it usually takes place at ambient temperature. In a conventional laundry washing operation, the 5 rinsing formulation is employed in the final rinse.

A particle dispersion is considered as being stable if no sedimentation, phase separation or development of turbidity is observed over time. This dispersion is destabilized when the particles undergo 10 aggregation with one another.

According to the invention the active substance (A) is considered as being destabilized in the rinsing medium (MR) comprising the vehicle (V) when the size of the objects in the dispersion is at least twice that of the 15 same objects in the absence of vehicle (V).

According to the invention the active substance (A) is in a solid or liquid organic or organosilicon material in particulate form which is insoluble in the medium (MAV), has an overall zero or 20 cationic charge in the medium (MAV), and remains insoluble in the rinsing medium (MR).

According to the invention the material constituting the active substance (A) is considered as being insoluble when less than 15%, preferably less than 10%, 25 of its weight is soluble in the medium (MAV) and the rinsing medium (MR).

Said material constituting the active substance (A) is in particulate soluble or liquid form. Preferentially it is in the form of an oil or a meltable solid (a wax for example).

5 Said particles may have an average diameter ranging from 10 nm to 200 μm , preferably from 10 nm to 5 μm and more preferably from 10 nm to 2 000 nm.
The diameter of said particles may be determined in well-known fashion by light scattering, by laser
10 diffraction or by microscopy.

Among the materials which may constitute the active substance (A) mention may be made in particular of those having a lubricating action which are capable of conferring on the textile fiber articles properties
15 of lubrication, which may be manifested in the provision of benefits such as softness, wrinkle resistance, ease of ironing, abrasion resistance, soil release, etc.

According to a first embodiment of the
20 invention said material constituting the active
substance (A) is an organosilicon material.

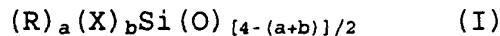
It is in particular a linear, cyclic, branched or crosslinked polyorganosiloxane resin, wax or oil.
Said polyorganosiloxane preferably has a dynamic
25 viscosity, measured at 25°C and at a shear rate of 0.01 Hz for a stress of 1 500 Pa (carried out on a Carrimed® of type CSL2-500), of between 10^4 and 10^9 cP.

According to the invention it is:

- a nonionic polyorganosiloxane
- a polyorganosiloxane having at least one cationic or potentially cationic function in the medium (MAV)
- 5 • an amphoteric polyorganosiloxane having at least one cationic or potentially cationic function in the medium (MAV) and at least one function which is neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR)
- 10 • a polyorganosiloxane having at least one function which is neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR).

Examples of polyorganosiloxanes that may be mentioned include

15 ➤ linear, cyclic or crosslinked polyorganosiloxanes formed of nonionic organosiloxane units of general formula



in which formula

20 - the symbols R are identical or different and represent a linear or branched alkyl hydrocarbon radical having 1 to 4 carbon atoms or an aryl radical, phenyl in particular;

- the symbols X are identical or different and represent a hydroxyl group, a linear or branched alkoxy radical having 1 to 12 carbon atoms, or a functional group OCOR', where R' represents an

25

alkyl group containing 1 to 12 carbon atoms,
preferably 1 carbon atom;

- a is 0, 1, 2 or 3
- b is 0, 1, 2 or 3
- 5 - a+b is 0, 1, 2 or 3

Preferentially said polyorganosiloxane is at least substantially linear, and very preferably is linear. By way of example mention may be made in particular of α - ω -bis(hydroxy)polydimethylsiloxane oils, α - ω -bis-
10 (trimethyl)polydimethylsiloxane oils, cyclic polydimethylsiloxanes, and polymethylphenylsiloxanes.

➤ linear, cyclic or crosslinked polyorganosiloxanes comprising per mole at least one ionic or nonionic organosiloxane unit of general formula

15
$$(R)_a(X)_b(B)_cSi(O)_{[4-(a+b+c)]/2} \quad (II)$$
 in which formula

- the symbols R are identical or different and represent a linear or branched monovalent alkyl hydrocarbon radical having 1 to 4 carbon atoms or
20 an aryl radical, phenyl in particular;
- the symbols X are identical or different and represent a hydroxyl group, a linear or branched alkoxy radical having 1 to 12 carbon atoms or a functional group OCOR', where R' represents an
25 alkyl group containing 1 to 12 carbon atoms, preferably 1 carbon atom;

- the symbols B are identical or different and represent an aliphatic and/or aromatic and/or cyclic hydrocarbon radical containing up to 30 carbon atoms, optionally interrupted by one or more oxygen and/or nitrogen and/or sulfur heteroatoms, optionally carrying one or more ether, ester, thiol, hydroxyl, optionally quaternized amine or carboxylate functions, the symbol B being linked to the silicon preferably by way of an Si-C- bond;
- a is 0, 1 or 2
- b is 0, 1 or 2
- c is 1 or 2
- a+b+c is 1, 2 or 3

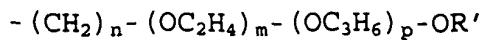
15 The other organosiloxane units present besides those of formula (II) are preferably nonionic and of formula (I) above.

Organosiloxane units having one or more strong anionic functions of sulfonate and/or phosphonate type may also

20 be present when the units of formula (II) are cationic or potentially cationic in the medium (MAV). They are present, however, in limited quantity, in order that said polyorganosiloxane has an overall zero or cationic charge in the medium (MAV).

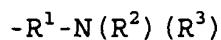
25 By way of example of substituents corresponding to the symbol (B) in the formula (II) above, mention may be made of

- polyether groups of formula



where n is 2 or 3, m and p are each from 0 to 30, and R' represents an alkyl radical containing 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms.

- primary, secondary, tertiary or quaternized amino groups, such as those of formula



where

10 * the symbol R¹ represents an alkylene group containing 2 to 6 carbon atoms, optionally substituted or interrupted by one or more nitrogen or oxygen atoms,

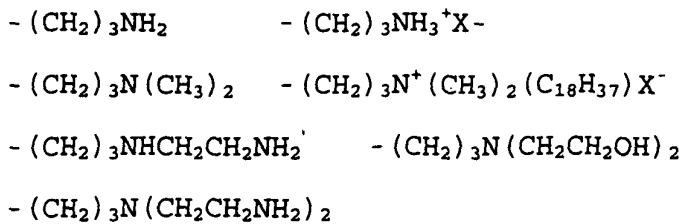
* the symbols R² and R³, identical or different, represent

15 • H,
• an alkyl or hydroxyalkyl group containing 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms,

20 • an aminoalkyl group, preferably primary, whose alkyl group contains 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms, optionally substituted and/or interrupted by at least one nitrogen and/or oxygen atom,

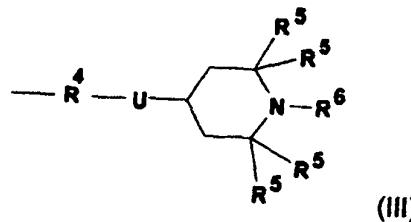
said amino group being optionally quaternized, for 25 example, by a hydrohalic acid or an alkyl or aryl halide.

Mention may be made in particular of those of formulae



5 Preferentially the polyorganosiloxanes which carry amino functions have in their chain, per 100 total silicon atoms, from 0.1 to 50, preferably from 0.3 to 10, and very particularly from 0.5 to 5 amino-functionalized silicon atoms.

10 - sterically hindered piperidyl groups of formula III

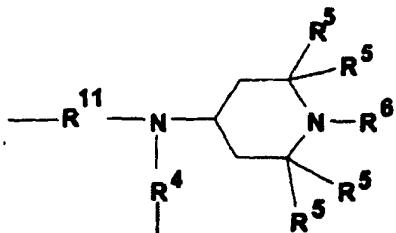


where

* R^4 is a divalent hydrocarbon radical selected
 15 from:
 ♦ linear or branched alkylene radicals
 having 2 to 18 carbon atoms;
 ♦ alkylene-carbonyl radicals whose
 alkylene moiety is linear or branched
 20 and contains 2 to 20 carbon atoms;
 ♦ alkylene-cyclohexylene radicals whose
 alkylene moiety is linear or branched
 and contains 2 to 12 carbon atoms and
 whose cyclohexylene moiety contains an

OH group and optionally 1 or 2 alkyl radicals having 1 to 4 carbon atoms;

- ◆ radicals of formula $-R^7-O-R^7$ in which the radicals R^7 are identical or different and represent alkylene radicals having 1 to 12 carbon atoms;
- ◆ radicals of formula $-R^7-O-R^7$ in which the radicals R^7 have the meanings indicated above and one of them or both are substituted by one or two -OH group(s);
- ◆ radicals of formula $-R^7-COO-R^7$ in which the radicals R^7 have the meanings indicated above;
- ◆ radicals of formula $-R^8-O-R^9-O-CO-R^8$ in which the radicals R^8 and R^9 are identical or different and represent alkylene radicals having 2 to 12 carbon atoms and the radical R^9 is optionally substituted by a hydroxyl radical;
- ◆ U represents $-O-$ or $-NR^{10}-$, R^{10} being a radical selected from a hydrogen atom, a linear or branched alkyl radical containing 1 to 6 carbon atoms, and a divalent radical of formula:



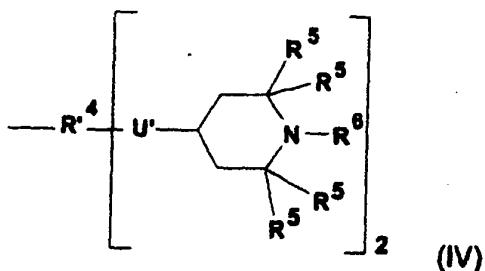
in which R^4 has the meaning indicated above, R^5 and R^6 have the meanings indicated below, and R^{11} represents a linear or branched divalent alkylene radical having 1 to 12 carbon atoms, one of the valence bonds (that of R^{11}) being connected to the atom of $-NR^{10}-$, the other (that of R^4) being connected to a silicon atom;

* the radicals R^5 are identical or different and are selected from linear or branched alkyl radicals having 1 to 3 carbon atoms and the phenyl radical;

* the radical R^6 represents a hydrogen radical or the radical R^5 or $O\bullet$.

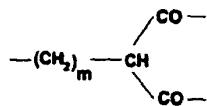
- or sterically hindered piperidyl groups of formula

IV



20 where

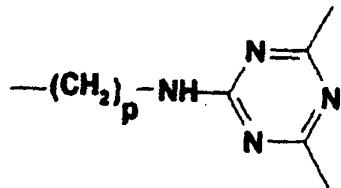
- ◆ R'^4 is selected from a trivalent radical of formula:



where m represents a number from 2 to

5 20,

and a trivalent radical of formula:



where p represents a number from 2 to

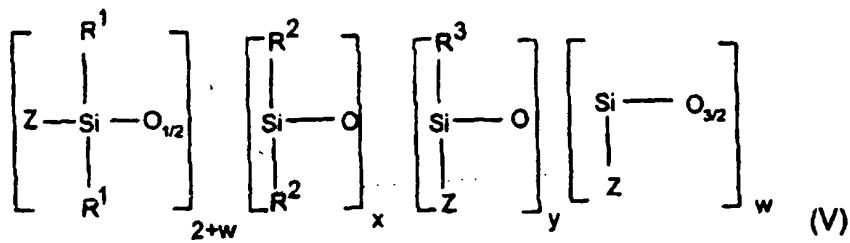
10 20;

- ◆ U' represents $-\text{O}-$ or $\text{NR}^{12}-$, R^{12} being a radical selected from a hydrogen atom and a linear or branched alkyl radical containing 1 to 6 carbon atoms;

15 R^5 and R^6 have the same meanings as those given above in relation to the formula III.

Preferentially said amino-functional polyorganosiloxanes are polyorganosiloxanes containing a sterically hindered piperidyl function, especially those which can be prepared by the process described in EP-A-659930.

Very preferably said polyorganosiloxane containing a sterically hindered amino function is a linear, cyclic or three-dimensional polyorganosiloxane of formula (V):



in which:

(1) the symbols Z, identical or different, represent R¹ below and/or B;

(2) the symbols R¹, R² and R³, identical and/or different, represent a monovalent hydrocarbon radical selected from linear or branched alkyl radicals having 1 to 4 carbon atoms, linear or branched alkoxy radicals having 1 to 4 carbon atoms, a phenyl radical and, preferably, a hydroxyl radical, an ethoxy radical, a methoxy radical or a methyl radical;

(3) the symbols B, functional groups which are identical and/or different, represent a group containing sterically hindered piperidyl function(s), selected from those mentioned above; and

(4) the number of units η Si without a group B is from 10 to 450, preferably from 50 to 250;

- the number of units η Si with a group B is from 1 to 5, preferably from 1 to 3;

- $0 \leq w \leq 10$ and $8 < y < 448$.

Very preferably said polyorganosiloxane is linear.

According to a second embodiment of the invention, said material constituting the active
5 substance (A) is an organic material.

By way of example mention may be made of

- mono-, di- or triglycerides of C₁-C₃₀ carboxylic acids or mixtures thereof, such as vegetable oils (colza oil, castor oil, sunflower oil, erucic rapeseed oil, linseed oil, etc.)
- sugar esters, sucroglycerides
- C₁-C₃₀ alcohol esters of C₁-C₃₀ carboxylic or C₂-C₃₀ dicarboxylic acids
- ethylene or propylene glycol monoesters or diesters of C₁-C₃₀ carboxylic acids
- propylene glycol C₄-C₂₀ alkyl ethers
- di(C₈-C₃₀ alkyl) ethers
- organic waxes comprising alkyl chains containing 4 to 40 carbon atoms. Among waxes mention may be made in particular of:
 - animal waxes (beeswax, lanolin, whale oil)
 - plant waxes (carnauba wax, candelilla wax, sugar cane wax, jojoba)
 - mineral waxes (montan, ozokerite, Utah wax)
- 25 • hydrocarbon waxes containing 4 to 35 carbon atoms (mineral oils, paraffins, microcrystalline waxes)

synthetic waxes such as polyolefins (polyethylene and polypropylene), sterone, and carbowax.

According to the invention the active 5 substance (A) is dispersed stably in the medium (MAV) by means of a surfactant (TAC).

Said surfactant (TAC) may be a nonionic surfactant and/or a cationic surfactant when the material constituting the active substance (A) is intrinsically 10 cationic or intrinsically potentially cationic in the medium (MAV).

Said surfactant (TAC) is a cationic surfactant or a mixture of cationic surfactant and nonionic surfactant when said material constituting the active substance 15 (A) is uncharged or has a zero charge; the amount of nonionic surfactant represents less than 70% of the weight of all of the surfactants (TAC).

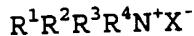
For effective realization of the invention the ratio of the mass of polymer constituting the 20 active substance (A) to the mass of surfactant (TAC) is from 0.01 to 10, preferably from 0.01 to 1.

The cationic charges generated by the optional cationic or potentially cationic functions of the active substance (A) and by the cationic surfactant 25 or surfactants at the surface of the active active substance (A) in dispersion in the medium (MAV) are such that the zeta potential of the active substance in

dispersion in (MAV) is from 0 to +50 mV, preferably from +10 to +40 mV.

Among cationic surfactants mention may be made in particular of the quaternary ammonium salts of

5 formula



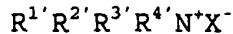
where

- R^1 , R^2 and R^3 , alike or different, represent H or an alkyl group containing less than 4 carbon atoms, 10 preferably 1 or 2 carbon atom(s), which is optionally substituted by one or more hydroxyl function(s), or may form, together with the nitrogen atom N^+ , at least one aromatic or heterocyclic ring,
- R^4 represents a C_8 - C_{22} , preferably C_{12} - C_{22} , alkyl or 15 alkenyl group, an aryl group or benzyl, and
- X^- is a solubilizing anion such as halide (for example, chloride, bromide or iodide), sulfate or alkyl sulfate (methyl sulfate), carboxylate (acetate, propionate or benzoate) or alkyl- or arylsulfonate.

20 Mention may be made in particular of dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and cetyltrimethylammonium bromide, stearylpyridinium chloride, Rhodaquat® TFR and Rhodamine® C15, sold by Rhodia, cetyltrimethylammonium chloride (Dehyquart ACA 25 and/or AOR from Cognis), and cocobis(2-hydroxyethyl)-ethylammonium chloride (Ethoquad C12 from Akzo Nobel).

Mention may also be made of other cationic surfactants having softening properties, such as:

- the quaternary ammonium salts of formula



5 where

- R^1' and R^2' , alike or different, represent H or an alkyl group containing less than 4 carbon atoms, preferably 1 or 2 carbon atom(s), which is optionally substituted by one or more hydroxyl function(s), or may 10 form, together with the nitrogen atom N^+ , a heterocyclic ring,
- R^3' and R^4' represent a C_8 - C_{22} , preferably C_{10} - C_{22} , alkyl or alkenyl group, an aryl group or benzyl, and
- X^- is an anion such as halide (for example, 15 chloride, bromide or iodide), sulfate or alkyl sulfate (methyl sulfate), carboxylate (acetate, propionate or benzoate) or alkyl- or arylsulfonate.

The following may be mentioned in particular: dialkyldimethylammonium chlorides such as ditallow 20 dimethylammonium chloride or methyl sulfate, etc., and alkylbenzyldimethylammonium chlorides.

- C_{10} - C_{25} alkylimidazolium salts such as C_{10} - C_{25} alkyl-imidazolinium methyl sulfates
- substituted polyamine salts such as N-tallow- 25 N,N',N' -triethanol-1,3-propylenediamine dichloride or dimethyl sulfate and N-tallow- N,N',N',N' -pentamethyl-1,3-propylenediamine dichloride

Among nonionic surfactants mention may be made of polyoxyalkenylated derivatives such as

- ethoxylated or ethoxy-propoxylated fatty alcohols
- ethoxylated or ethoxy-propoxylated triglycerides
- 5 - ethoxylated or ethoxy-propoxylated fatty acids
- ethoxylated or ethoxy-propoxylated sorbitan esters
- ethoxylated or ethoxy-propoxylated fatty amines
- ethoxylated or ethoxy-propoxylated di(1-phenyl-ethyl)phenols
- 10 - ethoxylated or ethoxy-propoxylated tri(1-phenyl-ethyl)phenols
- ethoxylated or ethoxy-propoxylated alkyl phenols

The dispersion medium (MAV) for the active substance (A) is an aqueous or aqueous-alcoholic polar medium.

Alcohols which may be present include ethanol, isopropanol, propylene glycol, butoxy ethanol, etc. These alcohols may represent up to 70% of the volume of medium (MAV)

20 Preferentially the medium (MAV) is water.

The medium may be brought to the desired pH of from 2 to 5 by addition of an acid, such as hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc.

The rinsing formulation (F) forming the 25 subject of the invention comprises a vehicle (V) which is capable of bringing the active substance (A) onto

the surface of the textile fiber articles in the rinsing operation.

According to the invention said vehicle (V)

- comprises an organic polymer which is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
- has an overall cationic or zero ionic charge in the medium (MAV)
- is capable, at the pH of the rinsing operation in the rinsing medium (MR), of developing anionic charges in sufficient quantity to destabilize the active substance (A) in the rinsing medium (MR).

15 Said organic polymer constituting the vehicle (V) may be any polymer which is soluble or dispersible in aqueous or aqueous-alcoholic medium with a pH of between 2 and 8 and which comprises at least one unit which is neutral in the medium (MAV) and potentially 20 anionic (HA) in the rinsing medium (MR).

They may further comprise at least one unit which is cationic or potentially cationic (HC) in the medium (MAV) and/or at least one hydrophilic or hydrophobic nonionic unit.

25 The term "dispersible" signifies that the vehicle (V) does not form a macroscopic precipitate in aqueous or aqueous-alcoholic medium.

Preferentially the polymer constituting the vehicle (V) is a copolymer comprising:

- at least one hydrophilic unit which is neutral in the medium (MAV) and potentially anionic
- 5 (HA) in the rinsing medium (MR) and
- at least one hydrophilic unit which is cationic or potentially cationic (HC) in the medium (MAV)
- and optionally at least one hydrophobic or
- 10 hydrophilic nonionic unit.

The polymer constituting the vehicle (V) may optionally contain anionic units (whose first pKa is less than 3), but in a very small amount, for example in an amount much less than 5% by weight relative to

15 the entirety of the units.

The relative amounts of the various units of the polymer constituting the vehicle (V) are such that in the medium (MAV) the overall charge of the polymer or copolymer is zero or cationic.

20 The relative amounts of vehicle (V) polymer, cationic surfactant (TAC), and material constituting the active substance (A) are such that in the course of the rinsing operation the number of anionic charges developed in the rinsing medium (MR) by the vehicle

25 polymer (V) is sufficient to destabilize the active substance (A) in the rinsing medium (MR), in particular

by electrostatic attraction with the surface charges of the active substance (A) in the medium (MR).

According to the invention the active substance (A) is considered as being destabilized in

5 the rinsing medium (MR) comprising the vehicle (V) when the turbidity of said medium reaches in less than 5 minutes a value at least 5 times greater than the turbidity that the same medium would have in the absence of vehicle (V).

10 The number of anionic charges developed in the rinsing medium (MR) by the vehicle (V) polymer to destabilize the active substance is preferably at least 1% relative to the number of cationic surface charges of the active substance (A) in the medium (MR).

15 This number of anionic charges may range up to 200% relative to the number of cationic surface charges of the active substance (A) in the medium (MR).

Possible examples that may be mentioned of polymers which may constitute the vehicle (V) include

20 in particular the polymers derived from ethylenically unsaturated monomers, and also natural polysaccharides and substituted or modified polysaccharides, and also mixtures of said polymers derived from ethylenically unsaturated monomers and said polysaccharides.

25 The term "polymer" is used here to denote both a homopolymer and a copolymer. The term copolymer

will be used when the polymer in question is derived from at least least two monomers of different type.

A first example of polymers which may constitute the vehicle (V) are the polymers derived:

5 • from at least one α - β monoethylenically unsaturated monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) and

10 • optionally at least one α - β monoethylenically unsaturated monomer which is cationic or potentially cationic (HC) in the medium (MAV), and

 • optionally at least one nonionic α - β monoethylenically unsaturated monomer which is hydrophilic or hydrophobic, preferably hydrophilic.

15 Preferentially the (V) is a random, block or graft copolymer derived

 • from at least one α - β monoethylenically unsaturated hydrophilic monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) and

 • from at least one α - β monoethylenically unsaturated hydrophilic monomer which is cationic or potentially cationic (HC) in the medium (MAV),

20 • and optionally from at least one nonionic α - β monoethylenically unsaturated monomer which is hydrophilic or hydrophobic, preferably hydrophilic.

The relative amounts of monomers from which (V) is derived are such that in the medium (MAV) the overall charge of the copolymer (V) is zero or cationic.

5 The average molar mass of said polymer or copolymer (V) derived from one or more α - β mono-ethylenically unsaturated monomers (measured by aqueous gel permeation chromatography (GPC) and expressed in polyoxyethylene equivalents) is greater than
10 5 000 g/mol, generally of the order of from 20 000 to 500 000 g/mol.

As examples of hydrophilic α - β mono-ethylenically unsaturated monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) mention may be made of

- monomers possessing at least one carboxyl function, such as α - β ethylenically unsaturated carboxylic acids or the corresponding anhydrides, such as acrylic, methacrylic, and maleic acid or anhydride,
20 fumaric acid, itaconic acid, N-methacryloylalanine, N-acryloylglycine and their water-soluble salts
- monomers which are precursors of carboxylic functions, such as tert-butyl acrylate, which give rise, after polymerization, to carboxylic functions
25 by hydrolysis.

As examples of hydrophilic α - β mono-ethylenically unsaturated monomer which is cationic or

potentially cationic (HC) in the medium (MAV) mention
may be made of

- acryloyl- or acryloyloxyammonium monomers such as trimethylammonium propyl methacrylate chloride,
- 5 trimethylammoniummethacrylamide or -methacrylamide chloride or bromide, trimethylammoniumbutyl-acrylamide or -methacrylamide methyl sulfate, trimethylammoniumpropylmethacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethyl-
- 10 ammonium chloride (APTAC), methacryloyloxyethyl-trimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride;
- 1-ethyl-2-vinylpyridinium or 1-ethyl-4-vinyl-pyridinium bromide, chloride or methyl sulfate;
- 15 • N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylamine chloride (DADMAC);
- polyquaternary monomers such as dimethylaminopropyl-methacrylamide chloride and N-(3-chloro-2-hydroxy-20 propyl)trimethylammonium (DIQUAT), etc.
- carboxybetaine monomers
- N,N-(dialkylamino- ω -alkyl)amides of α - β mono-ethylenically unsaturated carboxylic acids such as N,N-dimethylaminomethylacrylamide or
- 25 -methacrylamide, 2-(N,N-dimethylamino)ethyl-acrylamide or -methacrylamide, 3-(N,N-dimethylamino)propyl-acrylamide or -methacrylamide, and

4- (N,N-dimethylamino)butyl-acrylamide or
 -methacrylamide

- α - β monoethylenically unsaturated amino esters such as 2-(dimethylamino)ethyl methacrylate (DMAM), 5 3-(dimethylamino)propyl methacrylate, 2-(tert-butylamino)ethyl methacrylate, 2-(dipentylamino)ethyl methacrylate, and 2-(diethylamino)ethyl methacrylate
- monomers which are precursors of amine functions, such as N-vinylformamide, N-vinylacetamide, etc., 10 which give rise to primary amine functions by simple acid or base hydrolysis.

As examples of hydrophilic α - β mono-ethylenically unsaturated monomers which are uncharged or unionizable mention may be made of

- 15 • hydroxyalkyl esters of α - β ethylenically unsaturated acids, such as hydroxyethyl and hydroxypropyl acrylate and methacrylate, glyceryl monomethacrylate, etc.
- α - β ethylenically unsaturated amides such as 20 acrylamide, N,N-dimethylmethacrylamide, N-methylolacrylamide, etc.
- α - β ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylene segment of the polyethylene oxide type, such as polyethylene oxide 25 α -methacrylates (Bisomer S20W, S10W, etc., from Laporte) or α , ω -dimethacrylates, Sipomer BEM from Rhodia (ω - behenyl polyoxyethylene methacrylate), and

Sipomer SEM-25 from Rhodia (ω -tristyrylphenyl polyoxyethylene methacrylate), etc.

- α - β ethylenically unsaturated monomers which are precursors of hydrophilic units or blocks, such as 5 vinyl acetate, which, once polymerized, can be hydrolyzed in order to give rise to vinyl alcohol units or polyvinyl alcohol blocks
- α - β ethylenically unsaturated monomers of ureido type, and in particular 2-imidazolidinone-ethyl 10 methacrylamide (Sipomer WAM II from Rhodia).

By way of examples of hydrophobic nonionic α - β monoethylenically unsaturated monomers mention may be made of

- vinylaromatic monomers such as styrene, 15 vinyltoluene, etc.
- alkyl esters of α - β monoethylenically unsaturated acids, such as methyl and ethyl acrylate and methacrylate, etc.
- vinyl or allyl esters of saturated carboxylic acids, 20 such as vinyl or allyl acetates, propionates, and versatates.
- α - β monoethylenically unsaturated nitriles such as acrylonitrile, etc.

As examples of hydrophilic anionic α - β 25 monoethylenically unsaturated monomer (whose first pKa is less than 3) mention may be made of

- monomers possessing at least one sulfate or sulfonate function, such as 2-sulfoxyethyl methacrylate, vinylbenzene sulfonic acid, allyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, sulfoethyl acrylate or methacrylate, sulfopropyl acrylate or methacrylate and their water-soluble salts
- monomers possessing at least one phosphonate or phosphate function, such as vinylphosphonic acid, etc., the esters of ethylenically unsaturated phosphates, such as the phosphates derived from hydroxyethyl methacrylate (Empicryl 6835 from Rhodia) and those derived from polyoxyalkylene methacrylates, and their water-soluble salts.

15 By way of examples of polymers derived from ethylenically unsaturated monomers constituting the vehicle (V) mention may be made of:

- polyacrylic or polymethacrylic acids, alkali metal polyacrylates or polymethacrylates, preferably with a molar mass by weight of from 100 000 to 1 000 000 g/mol
- acrylic acid/DADMAC copolymers, with a molar ratio of 50/50 to 30/70, preferably with a molar mass by weight of from 70 000 to 350 000 g/mol
- 25 • acrylic acid/MAPTAC copolymers, with a molar ratio of 60/40 to 30/70, preferably with a molar mass by weight of from 90 000 to 300 000 g/mol

- acrylic acid/MAPTAC/linear C₄-C₁₈ alkyl methacrylate terpolymers comprising 0.005 to 10% by mass of alkyl methacrylate, with an acrylic acid/MAPTAC molar ratio ranging from 60/40 to 30/70, and preferably 5 having a molar mass by weight of from 50 000 to 250 000 g/mol
- acrylic acid/dimethylaminoethyl methacrylate (DMAEMA) copolymers, with a molar ratio of 60/40 to 30/70, preferably with a molar mass by weight of 10 from 50 000 to 300 000 g/mol.

A second example of polymers which can constitute the vehicle (V) are potentially anionic natural polysaccharides and potentially anionic or amphoteric substituted or modified polysaccharides.

15 The potentially anionic natural polysaccharides are formed of nonionic monosaccharide units and of monosaccharide units which are neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR), these units being alike or different. They 20 may be linear or branched.

More particularly said potentially anionic natural polysaccharides are branched polysaccharides formed

- of a main chain comprising alike or different 25 anhydrohexose units
- and of branches comprising at least one anhydropentose and/or anhydrohexose unit which is

neutral in the medium (MAV) and optionally potentially anionic in the rinsing medium (MR).

The hexose units (alike or different) of the main chain may be units of D-glucose, D- or L-
5 galactose, D-mannose, D- or L-fucose, L-rhamnose, etc.

The pentose and/or hexose units (alike or different) which are nonionic or neutral in the medium (MAV) and potentially anionic in the medium (MR) of the branches may be units of D-xylose etc., L- or D-
10 arabinose, D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, D-glucuronic acid, D-galacturonic acid, D-mannuronic acid, D-mannose substituted by a pyruvic group, etc.

By way of examples of natural polysaccharides
15 which are neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR) mention may be made of xanthan gum (such as the Rhodopol[®] products from Rhodia), succinoglycans, rhamsans, gellan gums, welan gums, etc.

20 Their molar mass by weight may range from 2 000 to 5 000 000, preferably from 10 000 to 5 000 000, more particularly from 10 000 to 4 000 000 g/mol.

The molar mass by weight Mw of said polysaccharides may
25 be measured by size exclusion chromatography.

When the polysaccharides in question are substituted or modified, their native skeleton is

formed of nonionic monosaccharide units and/or of monosaccharide units which are neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR), said monosaccharide units being alike or

5 different and being substituted or modified:

- by one or more groups which carry at least one charge which is neutral in the medium (MAV) and potentially anionic in the medium (MR)
- and optionally by one or more groups which carry 10 at least one charge which is cationic or potentially cationic in the medium (MAV),

the degree of substitution or modification of the monosaccharide units by the entirety of the groups which carry charges which are potentially anionic and 15 of optional groups which carry cationic charges being such that said substituted or modified polysaccharide is soluble or dispersible in aqueous or aqueous-alcoholic medium and has an overall cationic or zero charge in the medium (MAV).

20 Said substituted or modified polysaccharides may further comprise at least one nonionic modifying or substituent group.

Among the native skeletons which can be employed mention may be made of linear or branched 25 polysaccharides.

More particularly said polysaccharide is a substituted or modified branched polysaccharide whose native skeleton is formed

- of a main chain comprising alike or different
5 anhydrohexose units
- and of branches comprising at least one anhydropentose and/or anhydrohexose unit which is neutral in the medium (MAV) and optionally potentially anionic in the rinsing medium (MR),
- 10 the anhydrohexose and/or anhydropentose units of said polysaccharide being substituted or modified by one or more groups which carry at least one charge which is neutral in the medium (MAV) and potentially anionic in the medium (MR) and optionally at least one charge
- 15 which is cationic or potentially cationic in the medium (MAV),
the degree of substitution or modification DSi of the anhydrohexose and/or anhydropentose units by the entirety of said groups which carry charges which are
- 20 ionic or potentially ionic ranging from 0.01 to less than 3, preferably from 0.01 to 2.5,
with a ratio of the number of potentially anionic charges in the medium (MR) to the number of cationic or potentially cationic charges in the medium (MAV)
- 25 ranging from 100/0 to 30/70, preferably from 100/0 to 50/50.

When the polysaccharide in question is amphoteric the ratio of the number of charges which are potentially anionic in the medium (MR) to the number of charges which are cationic or potentially cationic in 5 the medium (MAV) is from 99.5/0.5 to 30/70, preferably from 99.5/0.5 to 50/50.

Said substituted or modified branched polysaccharide may further comprise at least one nonionic modifying or substituent group.

10 The molar mass by weight of said substituted or modified polysaccharides may range from 2 000 to 5 000 000, preferably from 10 000 to 5 000 000 g/mol. The molar mass by weight, M_w , of said polysaccharides may be measured by size exclusion chromatography.

15 When the polysaccharide in question carries substituent groups which are potentially anionic in the medium (MR) the measurement is made in water at a pH of 9-10 containing 0.1 M LiCl and 2/10 000 of sodium nitrate.

20 When the polysaccharide in question is amphoteric, i.e., carries substituent groups which are potentially anionic in the medium (MR) and groups which are cationic or potentially cationic in the medium. (MAV), the measurement is made in a 0.1 M aqueous 25 formic acid solution containing 0.05 M sodium nitrate and 10 ppm of high molar mass polyallyldimethylamine chloride (PDADMA) in the case of polysaccharides whose

DSi in terms of ionic or potentially ionic function is less than 0.5. For those whose DSi is greater than 0.5 a 0.025 M aqueous hydrochloric acid solution is used. The molar mass by weight, M_w , is established directly 5 in a known manner by means of the light scattering values.

The degree of substitution or of modification, DSi, corresponds to the average number of hydroxyl functions of the anhydrohexose and/or 10 anhydropentose units which are substituted or modified by said ionic or potentially ionic group or groups per anhydrohexose and/or anhydropentose unit.

Said ionic or potentially ionic groups are linked to the carbon atoms of the sugar skeleton either 15 directly or by way of $-O-$ bonds.

In the case of amphoteric polysaccharides the potentially anionic charges may be provided by modifying groups or substituent groups which are different from those which carry cationic or 20 potentially cationic charges; in that case said polymer is an amphotyte polysaccharide.

When a modifying group or substituent group at the same time carries a potentially anionic charge and a cationic or potentially cationic charge, said 25 polysaccharide is in that case of betaine type.

Said substituted or modified polysaccharide may further exhibit at least one nonionic modifying

group or substituent group. Said nonionic groups are attached to the carbon atoms of the sugar skeleton either directly or by way of -O- bonds. The presence of such groups is expressed in number of moles of

5 substitution MS, i.e., in average number of moles of precursor of said nonionic substituent which have reacted per anhydrohexose and/or anhydropentose unit.

If said precursor is not appropriate for forming new, reactive hydroxyl groups (alkylation precursor, for

10 example), the degree of substitution or of modification by the entirety of the ionic or ionizable groups and nonionic groups is less than 3 by definition.

If said precursor is capable of forming new, reactive hydroxyl groups (hydroxyl alkylation precursor, for

15 example), there is theoretically no limit on the number of moles of substitution, MS; it may, for example, be up to 6, preferably up to 2.

Among the groups which are potentially anionic in the medium (MR) mention may be made of those

20 containing one or more carboxylate (carboxylic) functions.

Mention may be made in particular of those of formula

- [-CH₂-CH(R)-O]_x- (CH₂)_y-COOH or

- [-CH₂-CH(R)-O]_x- (CH₂)_y-COOM

25 where

R is a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms

x is an integer ranging from 0 to 5

y is an integer ranging from 0 to 5

M represents an alkaline metal.

Very particular mention may be made of the
 5 carboxy groups $-\text{COO}^-\text{Na}^+$ attached directly to a carbon
 atom of the sugar skeleton and of carboxy methyl
 (sodium salt) groups $-\text{CH}_2\text{-COO}^-\text{Na}^+$ attached to a carbon
 atom of the sugar skeleton via an $-\text{O-}$ bond.

Among cationic or potentially cationic groups
 10 mention may be made of those which contain one or more
 amino, ammonium, phosphonium, pyridinium, etc.,
 functions.

Mention may be made in particular of the
 cationic or potentially cationic groups of formula

- 15 ■ $-\text{NH}_2$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-}(\text{CH}_2)_y\text{-COA-R'-N(R'')}_2$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-}(\text{CH}_2)_y\text{-COA-R'-N}^+(\text{R''})_3\text{ X}^-$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-}(\text{CH}_2)_y\text{-COA-R'-NH-R''''-N(R'')}_2$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-R'-N(R'')}_2$
- 20 ■ $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-R'-N}^+(\text{R''})_3\text{ X}^-$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-R'-NH-R''''-N(R'')}_2$
- $-\text{[-CH}_2\text{-CH(R)-O]}_x\text{-Y-R''}$

where

- R is a hydrogen atom or an alkyl radical
 25 containing 1 to 4 carbon atoms
- x is an integer ranging from 0 to 5
- y is a integer ranging from 0 to 5

- R' is an alkylene radical containing 1 to 12 carbon atoms, optionally carrying one or more OH substituents
- the radicals R'', which are alike or different, represent a hydrogen atom or an alkyl radical containing from 1 to 18 carbon atoms
- the radicals R''', which are alike or different, represent an alkyl radical containing 1 to 18 carbon atoms
- R''' is a linear, branched or cyclic alkylene radical containing 1 to 6 carbon atoms
- A represents O or NH
- Y is a heterocyclic aliphatic group containing 5 to 20 carbon atoms and one nitrogen heteroatom
- X⁻ is a counterion, preferably halide (chloride, bromide and iodide in particular), and N-alkylpyridinium-yl groups whose alkyl radical contains 1 to 18 carbon atoms, with a counterion, preferably halide (chloride, bromide and iodide in particular).

Among cationic or potentially cationic groups mention may be made very particularly of:

- those of formula
- NH₂
- CH₂-CONH- (CH₂)₂-N(CH₃)₂
- CH₂-COO- (CH₂)₂-NH- (CH₂)₂-N(CH₃)₂
- CH₂-CONH- (CH₂)₃-NH- (CH₂)₂-N(CH₃)₂

-CH₂-CONH-(CH₂)₂-NH-(CH₂)₂-N(CH₃)₂

-CH₂-CONH-(CH₂)₂-N⁺(CH₃)₃ Cl⁻

-CH₂-CONH-(CH₂)₃-N⁺(CH₃)₃ Cl⁻

- (CH₂)₂-N(CH₃)₂

5 - (CH₂)₂-NH-(CH₂)₂-N(CH₃)₂

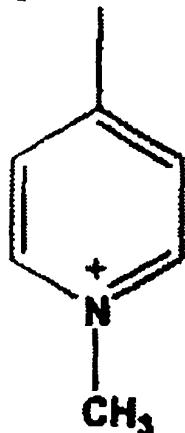
- (CH₂)₂-N⁺(CH₃)₃ Cl⁻

2-hydroxypropyltrimethyl ammonium chloride -CH₂-CH(OH)-

CH₂-N⁺(CH₃)₃ Cl⁻

- pyridinium-yl groups such as N-methyl pyridinium-yl

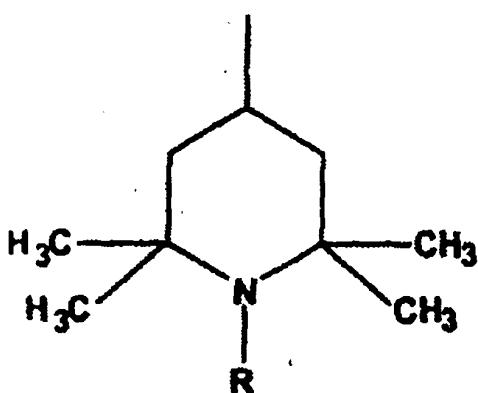
10 groups, of formula



with a chloride counterion

- hindered amino groups such as those derived from HALS

amines of general formula



15 where R represents CH₃ or H.

Among betaine groups mention may be made more particularly of the function of formula:

- $(\text{CH}_2)_2-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_2-\text{COO}^-$, an ethyldimethylammonium betaine function.

5 Among nonionic groups mention may be made of those of formula:

■ - $[-\text{CH}_2-\text{CH}(\text{R})-\text{O}]_x-\text{R}^1$ where

R is a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms

10 x is an integer ranging from 0 to 5

R^1 represents

■ a hydrogen atom
 ■ an alkyl radical containing 1 to 22 carbon atoms which is optionally interrupted by one or more

15 oxygen and/or nitrogen heteroatoms, cycloalkyl, aryl or arylalkyl, containing 6 to 12 carbon atoms

■ a radical $-(\text{CH}_2)_y-\text{COOR}^2$
 ■ a radical $-(\text{CH}_2)_y-\text{CN}$
 ■ a radical $-(\text{CH}_2)_y-\text{CONHR}^2$

20 where R^2 represents an alkyl, aryl or arylalkyl radical containing 1 to 22 carbon atoms,

and y is an integer ranging from 0 to 5

■ $-\text{CO}-\text{NH}-\text{R}^1$,

where R^1 is as defined above,

25 attached to a carbon atom of the sugar skeleton via an -O- bond.

Very particular mention may be made of the following groups:

- methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dodecyl, octadecyl, phenyl and benzyl, which are attached to a carbon atom of the sugar skeleton by way of ether, ester, amide or urethane linkage,
- cyanoethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl, which are attached to a carbon atom of the sugar skeleton by way of an -O- bond.

10 The hexose units (alike or different) of the main chain of the native skeleton may be units of D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, etc.

15 The pentose and/or hexose units (alike or different) which are nonionic or neutral in the medium (MAV) and potentially anionic in the medium (MR) of the branches of the native skeleton may be units of D-xylose, etc., L- or D-arabinose, D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, D-glucuronic acid, D-galacturonic acid, and D-mannuronic acid.

20 Examples of native skeleton that may be mentioned include galactomannanes, galactoglucomannanes, xyloglucans, xanthan gums, scleroglucans, 25 succinoglycans, rhamsans, welan gums, etc.

25 Preferentially the native skeleton is a galactomannan.

The galactomannanes are macromolecules containing a main chain of D-mannopyranose units attached in β (1-4) position which is substituted by D-galactopyranose units in α (1-6) position. Among these mention may be 5 made of guar gum, carob gum, and tara gum.

Very preferentially the native skeleton is a guar gum. Guar gums have a mannose/galactose ratio of 2.

The substituted or modified polysaccharides used according to the invention may be obtained by 10 functionalizing the native skeleton by means of precursors of the ionic or potentially ionic groups and optionally nonionic groups.

These operations of functionalization may be carried out in a known way by oxidation, substitution, 15 condensation, and/or addition.

Examples of substituted or modified polysaccharides which can be used according to the invention include

- carboxymethylgalactomannans, especially 20 carboxymethylguars,
- carboxymethylhydroxypropylgalactomannans, especially carboxymethylhydroxypropylguars,
- carboxymethyl-hydroxypropyltrimethylammonium chloride galactomannans, especially carboxymethyl- 25 hydroxypropyltrimethylammonium chloride guars,
- carboxymethylhydroxypropyl-hydroxypropyltrimethylammonium chloride galactomannans, especially

carboxymethyl-hydroxypropyl-hydroxypropyltrimethyl-ammonium chloride guars.

When the vehicle (V) is a polysaccharide it is preferable for the dispersion of the active 5 substance (A) in the medium (MAV) comprising the vehicle (V) to have a pH ranging from 3.5 and in particular from 4.5 to 5 when said polysaccharide is a substituted or modified guar.

For effective realization of the invention 10 the amount of vehicle (V) present in the formulation according to the invention is from 0.001 to 5 parts by weight, preferably from 0.01 to 4 parts, and more particularly from 0.05 to 2 parts by weight per 100 parts by weight of active substance (A).

15 The formulation (F) according to the invention may be in the form

- of a stable dispersion (liquid, cream, paste, gel, etc)
- or in solid form (powder, granules, block, tablet, 20 etc).

The formula (F) in the form of a stable dispersion may be obtained by

- 1) preparing an aqueous dispersion (emulsion, microemulsion, suspension) of the material 25 constituting the active substance (A) with the aid of a surfactant (TAC) as stabilizer;

- 2) optionally diluting with water or a water/alcohol mixture (depending on the desired proportion of active substance A in the formulation F) and adjusting the pH to a value of 5 2.5 - 5 using an acid (hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc);
- 3) adding the vehicle (V) to the resulting dispersion;
- 4) optionally adding an additional amount of 10 surfactant (TAC) before or after adding said vehicle, and
- 5) if necessary readjusting the pH to a value of from 2.5 - 5 using an acid.

For effective realization of the invention 15 the aqueous or aqueous-alcoholic formulation (F) comprises per 100 parts of its weight:

- from 0.01 to 40, preferably from 0.05 to 30 parts by dry weight of active substance (A)
- from 0.01 to 50, preferably from 0.01 to 35 parts 20 by dry weight of cationic surfactant (TAC)
- from 0.001 to 4, preferably from 0.01 to 1 part by dry weight of vehicle (V) polymer.

Said dispersion may have a solids content of from 0.021 25 to 90%, preferably from 0.07 to 51% by weight.

The formulation (F) in the form of a solid 25 may be obtained by

- 1) preparing an aqueous dispersion of polymer constituting the active substance (A) with the aid of a surfactant (TAC) as stabilizer;
- 2) adjusting the pH to a value of 2.5 - 5 using an acid (hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc);
- 3) adding the vehicle (V) to the resulting dispersion;
- 4) optionally adding an additional amount of surfactant (TAC) before or after adding said vehicle, and
- 5) if necessary readjusting the pH to a value of from 2.5 - 5 using an acid;
- evaporating/drying.

15 The evaporating/drying step may be carried out in accordance with any means known to the skilled worker, in particular by lyophilization (i.e., freezing, then sublimation) or, preferably, by spray drying. Spray drying may be carried out in any known apparatus, 20 such as a spraying tower in combination with a spraying operation carried out by a nozzle or a turbine with a stream of hot air. The implementation conditions are dependant on the type of atomizer used; these conditions are generally such that the temperature of 25 the entirety of the product in the course of drying is at least 30°C and does not exceed 150°C.

The evaporating/drying step may be facilitated by the presence within the dispersion which is subjected to said step of a protectant, in particular by the presence of at least one sugar, saccharide or

5 polysaccharide which is water-soluble or water-dispersible, preferably a sugar. The amount of protectant may represent of the order of from 10 to 50 parts by weight per 100 parts by weight of active substance (A).

10 Among sugars mention may be made of aldoses such as glucose, mannose, galactose, and ribose and of ketoses such as fructose.

The granules obtained may be ground to give a powder or compacted conventionally to give tablets, for example.

15 The formulation (F) may further comprise other, customary constituents of cationic rinsing formulations.

It may in particular comprise at least one cationic and/or nonionic softener, such as acyclic

20 quaternary ammonium compounds, alkoxyolated polyamines, quaternary diamido ammonium salts, quaternary ammonium esters, quaternary imidazolium salts, primary, secondary or tertiary amines, alkoxyolated amines, cyclic amines, nonionic sugar derivatives, etc., which

25 are mentioned in particular in WO 00/68352. Examples of some of these cationic softeners have already been mentioned earlier on as surfactant (TAC).

The softeners may be present in a proportion of from 0.5 to 90%, preferably from 0.5 to 40%, depending on the concentration of said formulation (F).

Also present may be:

- 5 - optical brighteners (0.1 to 0.2%)
- color transfer inhibitors (polyvinylpyrrolidone, polyvinyloxazolidone, polymethacrylamide, etc. 0.03 to 25%, preferably 0.1 to 15%)
- water-soluble monovalent mineral salts, such as
- 10 sodium, potassium or ammonium chlorides, nitrates or sulfates (especially when the vehicle (V) is a polysaccharide), in a proportion, for example, of from 0.01 to 2 mol per liter
- dyes,
- 15 - fragrances,
- foam suppressants
- enzymes
- bleaches.

The formulation (F) of the invention may be 20 employed to carry out a rinsing operation which follows an operation of washing - by hand or in a washing machine - textile fiber articles. Said articles may consist of natural and/or artificial and/or synthetic fibers.

25 Said formulation is especially advantageous for rinsing cotton or cotton-based articles.

It may be employed in the rinsing bath in a proportion of from 0.001 to 5 g/l, preferably from 0.005 to 2 g/l, the proportion of formulation being expressed in terms of dry matter. This rinsing operation may be carried 5 out at ambient temperature.

This rinsing operation makes it possible to impart to said articles, in addition to the conventional benefits of softness which are provided by the nonionic and/or cationic softener or softeners, 10 properties of wrinkle resistance (antiwrinkle properties) and/or of ease of ironing, of abrasion resistance, and soil release properties, which are provided by the deposition of the active substance (A) on the surface of said articles, this deposition being 15 promoted by the presence of the vehicle (V).

Advantageous soil release properties are provided in particular through the use as active substance (A) in the formulation (F) of a silicone oil, in particular of a silicone oil containing a hindered piperidyl 20 function.

The invention secondly provides a process for treating textile fiber articles by contacting said articles in the course of a rinsing operation in aqueous or aqueous-alcoholic medium with the rinsing 25 formulation (F) as described above, then recovering said rinsed articles.

The operating conditions of such a treatment have already been mentioned above.

The invention thirdly provides a process for enhancing the antiwrinkle and/or easy-iron and/or soil release and/or abrasion resistance properties of textile fiber articles which consists in contacting said articles in the course of a rinsing operation in aqueous or aqueous-alcoholic medium with the rinsing formulation (F) as described above, then in recovering 10 said rinsed articles.

The operating conditions for carrying out such a process have already been mentioned above.

The invention fourthly provides for the use in a formulation (F) intended for use in an operation of rinsing (R) textile fiber articles (S) by means of an aqueous or aqueous-alcoholic medium (MR), 15 formulation (F) comprising at least one active substance (A) comprising at least one liquid or solid organic or organosilicon material in particulate form 20 and being

- in the form of a stable dispersion with a pH of from 2 to 5 of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) or
- in a solid form obtained by drying said 25 dispersion,

the nature of the active substance (A) and of the aqueous or aqueous-alcoholic medium (MAV) being such that the active substance (A)

- is insoluble in the medium (MAV)
- 5 ▪ has an overall zero or cationic charge in the medium (MAV),
- is stabilized in the medium (MAV) by means of a cationic surfactant (TAC), it being possible for said cationic surfactant (TAC) to be wholly or 10 partly replaced by a nonionic surfactant when the material constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV)
- remains insoluble in the rinsing medium (MR);
- 15 of at least one organic polymer which
 - ♦ is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
 - ♦ has an overall cationic or zero ionic charge in the medium (MAV)
- 20 ♦ and is capable, at the pH of the rinsing operation in the rinsing medium (MR), of developing anionic charges in sufficient quantity to destabilize the active substance (A) in the rinsing medium (MR);
as a vehicle (V) capable of bringing said active
- 25 substance (A) toward the surface of said textile fiber articles (S) in the rinsing operation (R).

The nature and the relative amounts of the various constituents, their conditions of use, and the operating conditions to be employed have already been set out above.

5 The object fifthly provides a process for enhancing the deposition of an active substance (A) comprising at least one solid or liquid organic or organosilicon material in particulate form on the surface of textile fiber articles (S), during an

10 operation of rinsing of said articles by means of an aqueous or aqueous-alcoholic medium (MR) obtained from a formulation (F) comprising said active substance (A), the formulation (F) being

 - in the form of a stable dispersion with a pH of

15 from 2 to 5 of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) or

 - in a solid form obtained by drying said dispersion,

 the nature of the active substance (A) and of the

20 aqueous or aqueous-alcoholic medium (MAV) being such that the active substance (A)

 • is insoluble in the medium (MAV)

 • has an overall zero or cationic charge in the medium (MAV),

25 • is stabilized in the medium (MAV) by means of a cationic surfactant (TAC), it being possible for said cationic surfactant (TAC) to be wholly or

partly replaced by a nonionic surfactant when the material constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV)

5 ♦ remains insoluble in the rinsing medium (MR) ;
by adding to said formulation (F) a vehicle (V)
comprising at least one organic polymer which
♦ is soluble or dispersible in the medium (MAV) and
in the rinsing medium (MR)
10 ♦ has an overall cationic or zero ionic charge in
the medium (MAV)
♦ and is capable, at the pH of the rinsing operation
in the rinsing medium (MR), of developing anionic
charges in sufficient quantity to destabilize the
15 active substance (A) in the rinsing medium (MR) .

The nature and the relative amounts of the various constituents, their conditions of use and the operating conditions to be employed have already been set out above.

20 The examples which follow are given by way of illustration.

Example 1: Antiwrinkle and easy-iron effect

30% of a sunflower oil of type Lubrirob[®] TOD18.80 (from Rhodia/Novance) is emulsified in water in a
25 microfluidizer (4 bar, 3 cycles) with heating (50°C) in
the presence of 3% by weight of cationic surfactants
(cetyltrimethylammonium bromide type) .

This gives an emulsion (E) having a dry extract of 30% by weight of active substance, whose size, measured by laser diffraction (Horiba granulometer), is 250 nm.

This size is a mass-average size of the size
5 distribution of the emulsion.

This emulsion (E) is used to produce various
formulations.

Formulation I1

The pH of the emulsion (E) is adjusted to 4.0 with 1 N
10 hydrochloric acid solution. The resulting dispersion is
milky.

Under mechanical stirring 20 ml of the dispersion are
poured into 1 ml of water whose pH has been adjusted to
4. This gives a mixture, pH = 4, whose appearance is
15 not significantly different from that of the original
dispersion. This mixture is stable for a number of
days, does not form any precipitate and does not change
in turbidity over time.

Formulation III

20 The pH of the emulsion (E) is adjusted to 4.0 with 1 N
hydrochloric acid solution. The resulting dispersion is
milky.

Also prepared is a 2.2% by weight aqueous solution of a
1:1 molar acrylic acid-DADMAC copolymer (with a molar
25 mass of 100 000 g/mol) (vehicle V), the solution having
been adjusted to a pH of 4.0 with 10% by weight
hydrochloric acid solution.

20 ml of the dispersion of active substance (A) are poured into 1 ml of the vehicle (V) copolymer solution under mechanical stirring. This gives a mixture with a pH of 4 whose appearance is not significantly different 5 from that of the original dispersion. This mixture is stable for a number of days, does not form any precipitate and does not change in turbidity over time.

Dilute formulations II(a) and III(a) obtained by diluting formulations II and III in water at a pH of 4

10 A Horiba granulometer vessel is introduced with water whose pH has been adjusted to 4 (approximately 100 ml). 0.1 ml of the formulation II is added to the vessel under mechanical stirring and the change in size of the emulsion over time is monitored.

15 The same operation is repeated with 0.1 ml of formulation III.

The results are given in table 1.

Table 1:

Time (min)	Size of the emulsion in nm	
	Formulation II(a)	Formulation III(a)
1	525	525
5	525	525
10	525	525

This size does not change over time.

Dilute formulations II(b) and III(b) obtained by
diluting formulations II and III in water at a pH of
7.2

The granulometer vessel is charged with water at its
 5 natural pH of 7.2 (approximately 100 ml).

0.1 ml of the formulation II is added therein under
 mechanical stirring and the change in size of the
 emulsion over time is monitored.

The same operation is repeated with 0.1 ml of
 10 formulation III.

The results are given in table 2.

Table 2

Time (min)	Size of the	Size of the
	emulsion in nm Formulation II(b)	emulsion in nm Formulation III(b)
1	525	750
5	525	1230
10	525	1800

Effect of the (V)/(A) weight ratio: amount of vehicle
(V)/amount of active substance (A)

15 The pH of the emulsion (E), containing 30% by weight of
 active substance, is adjusted to 4.0 with 1 N
 hydrochloric acid solution. The dispersion obtained is
 milky.

Also prepared is an 11% by weight aqueous solution of a
 20 1:1 molar acrylic acid-DADMAC copolymer (with a molar
 mass of 100 000 g/mol) (vehicle V), the pH of the

Washing machine test

The following three rinsing formulations are prepared or employed:

- * 50 ml of a commercial softener formulation FR,
- 5 containing only cationic surfactants (15% solids)
- * a softener formulation FRII obtained by adding 10 ml of the formulation II above, of pH = 4, to 50 ml of the formulation FR, corresponding to 196 mg of active substance (A) per liter of water in the machine
- 10 * a softener formulation FRIII obtained by adding 10 ml of the formulation III above, of pH = 4, to 50 ml of the formulation FR, corresponding to 190 mg of active substance (A) per liter of water in the machine.

1.5 kg of flat cotton fabric samples

- 15 measuring 50 cm x 50 cm (their finish having been removed beforehand by three successive washes with demineralized water at 90°C) are washed at 30°C using a commercial powder detergent formulation in a Miele® washing machine (from Miele).

- 20 At the end of the wash cycle one of the samples is placed in reserve and rinsed with 15 liters of mains water at 23°C, then wrung; the rinse cycle lasts 5 minutes. The other samples are divided into three batches.

- 25 The first batch is rinsed for 5 minutes with 15 liters of mains water at 23°C, to which 50 ml of formulation FR

have been added, then is wrung under the same conditions as the reserved sample.

The second batch is rinsed for 5 minutes with 15 liters of mains water at 23°C, to which 60 ml of formulation

5 FRII1 have been added, then is wrung under the same conditions as the reserved sample.

The third batch is rinsed for 5 minutes with 15 liters of mains water at 23°C, to which 60 ml of formulation

FRIII1 have been added, then is wrung under the same

10 conditions as the reserved sample.

During the rinse cycle the pH of the medium reaches 7.

After wringing, the articles are placed on a rack to dry.

After drying, a digital color photograph is

15 taken of an area of the dry samples, which is subsequently converted into 256 levels of grey (grey scale from 0 to 255).

The number of pixels corresponding to each level of grey is counted.

20 For each resulting histogram the standard deviation σ of the distribution of the level of grey is measured. If wrinkling is substantial, the distribution of the level of grey is large.

σ_1 corresponds to the standard deviation corresponding

25 to the reserved sample (rinsed without a rinsing formulation).

σ_2 corresponds to the standard deviation obtained with the rinsing formulation in question.

σ_3 corresponds to the standard deviation obtained on flat starting samples which have not undergone an 5 operation of washing, rinsing or wringing.

The performance value WR (wrinkle recovery) is given by the following equation

$$WR(\%) = [(\sigma_1 - \sigma_2) / \sigma_1] f \times 100$$

where f is a standardization factor, equal to $1 / [(\sigma_1 - 10 \sigma_3) / \sigma_1]$

A value of:

- 0% corresponds to zero benefit
- 100% corresponds to a flat surface

15 The results of the wrinkle test are as

follows:

Rinsing formulation	FR	FRII(a)	FRIII(a)
WR	30%	38%	52%

The above results show that the addition of the vehicle (V) enhances the deposition of the active substance (A) on the fabric, which manifested in an 20 improvement in the antiwrinkle effect of the active substance (A).

Example 2: Soil release effect

Formulation I2

An emulsion is used which comprises 30% by weight of 25 silicone containing hindered piperidyl functions

(Rhodorsil[®] 21645 from Rhodia) and 3% of a nonionic surfactant of ethoxylated fatty alcohol type (Symperonic A7).

Under mechanical stirring, 20 ml of the dispersion are 5 poured into 1 ml of water whose pH has been adjusted to 4.5.

0.1 g of sodium chloride is added (for better comparison with formula II2 below).

Formulation II2

10 An emulsion is used which comprises 30% by weight of silicone containing hindered piperidyl functions (Rhodorsil[®] 21645 from Rhodia) and 3% of a nonionic surfactant of ethoxylated fatty alcohol type (Symperonic A7).

15 Also prepared is a 1% by weight solution of xanthan gum (Rhodopol[®] T from Rhodia) with a molar mass by weight of 4 000 000 g/mol in water with a pH of 4.5.

Under mechanical stirring, 20 ml of the dispersion are poured into 1 ml of the xanthan gum solution. The final 20 dispersion has a pH of 4.5.

0.1 g of sodium chloride is added to stabilize the dispersion over time.

Test

The test is carried out in a Tergotometer 25 laboratory apparatus which is well known to the formulators of detergent compositions. The apparatus simulates the mechanical and thermal effects of the

American-type washing machines with a pulsing action; by virtue of the presence of 3 washing pots, it allows series of simultaneous tests to be carried out with a considerable time saving.

5 The composition of the laundry detergent employed is as follows:

Composition of the laundry detergent	Parts by weight
Zeolite 4A	25
Light carbonate	15
Disilicate R2A	5
Acrylic/maleic copolymer Sokalan CP5 (BASF)	5
Na sulfate	9.5
Carboxymethylcellulose	1
Perborate monohydrate	15
Tetraacetylenediamine	5
Linear dodecylbenzenesulfonate	6
Synperonic A3 (C12-C15 fatty alcohol ethoxylated with 3 EO)	3
Synperonic A9 (C12-C15 fatty alcohol ethoxylated with 9 EO)	9
Enzyme esperase 4.0 T	0.5
Fragrances	1

The following three rinsing formulations are tested:

- * 7 ml of a commercial softener formulation FR containing only cationic surfactants (15% solids)

- * a softener formulation FRI2 obtained by adding 0.3 ml of the formulation I2 above to 7 ml of the formulation FR,
- * a softener formulation FRII2 obtained by adding 5 0.3 ml of the formulation II2 above to 7 ml of the formulation FR.

(a) Prewash/rinsing/drying:

6 test specimens measuring 10 x 10 cm and made of flat woven cotton are prewashed in a Tergotometer for 20 10 minutes at 23°C with the above laundering formula; the water used has a hardness of 30°HT (diluted Contrexéville[®] mineral water); the amount of laundry detergent employed is 5 g per liter of water; the number of test specimens per pot is 6.

15 The squares of fabric are subsequently rinsed 3 times for 5 minutes (each time), twice with cold water and the third time with cold water to which either 7 ml of commercial rinsing formula FR or 7.3 ml of the rinsing formulas FRI2 or FRII2 have been added.

20 The squares of fabric are subsequently wrung out and then dried on clotheshorses.

(b) Staining:

4 drops of dirty motor oil (DMO) are deposited on the test specimens prewashed as above.

25 To ensure good fixing of the stains, the soiled fabrics are placed in an oven at 60°C for 1 hour.

To allow effective reproducibility of the results, the fabrics are washed within 24 hours.

(c) Washing/rinsing/drying:

The soiled tests specimens are washed, rinsed, wrung and dried under the same conditions as those described in (a).

Evaluation

The reflectance of the fabrics before and after washing is measured using a Dr. Lange/Luci 100 colorimeter.

10 The efficacy of the test polymer as a soil release agent is evaluated by the percentage elimination of the stains, calculated by the formula

$$E \text{ in \%} = 100 \times (R_3 - R_2) / (R_1 - R_2)$$

where

15 R_1 represents the reflectance before washing of the unsoiled fabric (step (a))

R_2 represents the reflectance before washing of the soiled fabric (steps (a) and (b))

20 R_3 represents the reflectance after washing of the soiled fabric (steps (a), (b) and (c))

For each test product the mean percentage stain elimination is calculated.

The results obtained are as follows:

Rinsing formulation	Cotton E in %
FR	55
FRI2	61
FRII2	68

A significant enhancement of the removal of stains of the dirty motor oil type is observed when xanthan gum is employed as vehicle.